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GROUND STATE ENERGY OF A MOLECULE

IN THE ADIABATIC APPROXIMATION

by

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The Ground State Energy of a Molecule in the Adiabatic Approximation[*]

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In a recent paper under this title, Brattsev[1] has offered a proof that the energy of the ground state of a molecule (accurately) calculated in the Adiabatic Approximation is a <u>lower</u> bound to the true energy of the ground state. The purpose of the present note is two fold: First to correct a slight logical flaw in the proof, and secondly, to materially simplify the proof.

The difficulty with Brattsev's proof is that he apparently has not separated off the motion of the center of mass of the system. Thus his Ψ is in fact a continuum wave function and therefore is <u>not</u> normalizeable, contrary to what he states. As is well known there are many ways of splitting off the motion of the center of mass.[2] For definiteness sake, let us suppose we have referred the nuclear coordinates and the electronic coordinates to the center of mass of the nuclei. Then we may write the <u>internal</u> Hamiltonian[3] as

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$$H = T_R + T_r + V(r,R) \tag{1}$$

where T_R is the kinetic energy of the nuclei relative to their center of mass, T_r is the kinetic energy of the electrons relative to the center of mass of the nuclei, and $V(r,R)$ is the potential energy.

The Adiabatic Approximation to the solution of $H\psi = E\psi$ then reduces to the successive solution of the two equations

$$(T_r + V)\phi = \mathcal{E}(R)\phi \tag{2}$$

$$(T_R + \mathcal{E}(R))\varphi = E_A \varphi \tag{3}$$

and we want to show[4] that

$$E \geqslant E_A \tag{4}$$

To do this we note that

$$E(\psi, \psi)_{R,r} = (\psi, H\psi)_{R,r} \tag{5}$$

where we have put the subscripts on the scalar product symbol to remind ourselves that we are to integrate over both electronic (and sum over spins) and nuclear coordinates. We now observe that for fixed R

$$(\psi , (T_r + V) \psi)_r \;\geqslant\; \mathcal{E} (R) (\psi , \psi)_r \qquad (6)$$

by the variational principle for equation (2). This then implies from (1) and (5) that

$$E(\psi , \psi)_{R,r} \;\geqslant\; (\psi , (T_R + \mathcal{E} (R)) \psi)_{R,r} \qquad (7)$$

But now for fixed r

$$(\psi , (T_R + \mathcal{E} (R)) \psi)_R \;\geqslant\; E_A (\psi , \psi)_R \qquad (8)$$

by the variational principle for equation (3), whence (7) becomes

$$E \;\geqslant\; E_A$$

which is what we set out to prove.

FOOTNOTES

1. V. F. Brattsev, Dokl. Akad. Nauk. SSSR $\underline{160}$, 570 (1965) (English translation: Sov Phys.-Dokl. $\underline{10}$, 44 (1965)).

2. See for example Jepsen and Hirschfelder, Proc. Nat. Acad. Sci. U.S.A. $\underline{45}$, 249 (1959) and J. Chem. Phys. $\underline{32}$, 1323 (1960).

3. We are using the same symbols as in reference 1 but with a slightly altered meaning.

4. As will be seen, the essential ingredient in the proof is that each term in H occurs in one and only one of the equations (2) and (3). This observation then permits ready generalization of the result (-) to other ways of separating the center of mass and other ways of defining the Adiabatic Approximation.